SUMMARY

A stereocomplex is formed by mixing isotactic and syndiotactic poly(methyl methacrylate) (it- and st-PMMA) under suitable circumstances. This thesis describes the investigation of the structure of this stereocomplex. The final result is a model consisting of a double-stranded helix in which the nearly extended isotactic chain is surrounded by the syndiotactic chain.

In *Chapter 2* the composition of the stereocomplex was determined. The two polymers were mixed in bulk as well as in very dilute solution at different it/st ratios. With the aid of differential scanning calorimetry and X-ray diffraction it was established that the same stereocomplex is always formed. Osmometry, viscometry and turbidimetry on very dilute solutions as well as differential scanning calorimetry on bulk mixtures, all pointed to the composition of the stereocomplex of it/st = 1/2. The double-stranded helix model is constructed in such a way that the st-PMMA encompasses the it-PMMA whereby twice the amount of st-PMMA is needed with respect to it-PMMA.

By investigating the complexing ability of other polyalkylmethacrylates (in *Chapter 3*) it was possible to determine what ester groups are allowed in the stereocomplex. It appeares that the isotactic chain has to be a methyl ester; it-poly(methacrylic acid) and it-poly(ethyl methacrylate) are not able to associate with a syndiotactic chain under any circumstances. However, it-poly(methyl methacrylate) can form a stereocomplex with either st-poly(methyl methacrylate), or st-poly(methacrylic acid) or even st-poly(isobutyl methacrylate). Clearly, in the double-stranded helix model modification of the inner (isotactic) chain will have a greater influence on complex formation than modification of the outher (syndiotactic) chain.

High resolution n.m.r. (see *Appendix*) applied to very dilute solutions and the solid state showed that the chemical shift as well as the spin-lattice relaxation times in the stereocomplex an
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PMMA should be 16
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stereocomplex and in the pure components are nearly the same. Hence, no specific interactions occur in the stereocomplex. The stability of the stereocomplex is caused mainly by a good spatial fit between the two stereoregular polymers.

A good model of the stereocomplex should consist of chains with a low conformational energy, while the stabilization energy caused by stereocomplex formation must be rather large. From X-ray data, the pitch and the screw-symmetry of the helix were determined. With these data the geometrical parameters and the conformational energies are estimated with the aid of the virtual bond method *(Chapter 4)*. Next the stabilization energy is calculated. As two contiguous PMMA monomeric units can differ in conformation and configuration the residue of the helix was composed of two monomeric units.

Using this method, the crystal structure of it-PMMA is investigated first *(Chapter 5)*. In the literature a double-stranded helix was proposed. This idea was also disputed. However, our results confirm a double-stranded 10/1 helix. From X-ray diffraction data the unit cell proved to be triclinic.

Finally, the virtual bond method was applied to the stereocomplex *(Chapter 6)*. From the few data of the X-ray diffraction pattern and by the comparison with it-PMMA, st-PMMA, and the stereocomplex of it-PMMA and st-poly(methacrylic acid), it was established that the pitch of the helix is 18.4 Å and the screw-symmetry of it-PMMA is about 8/1. As the composition of the stereocomplex is it/st = 1/2, the screw symmetry of st-PMMA should be 16/1. The final results lead to a double-stranded helix, consisting of an isotactic 30/4 helix of it-PMMA and a 60/4 helix of st-PMMA, the exact fiber period being 4 × 18.4 = 73.6 Å. The stability of this double-stranded helix is very high. However, the relative positions of different double-stranded helices with respect to each other in the crystallites is rather disorderly and the size of crystallites is only about 50 Å. In pure it-PMMA as well as in the stereocomplex the feasibility of screwing the helices easily through one another, could be an explanation of the formation of the double-stranded helices.